Theoretical Insights of Metallic Ag Growth on α-Ag_2WO_4 upon Electron Irradiation

Miguel A. San-Miguel[a], Juan Andrés[b], Elson Longo[c], Edison Z. da Silva[d]

[a] *Instituto de Química, Unicamp, Campinas 13083-970, Brazil – smiguel@iqm.unicamp.br*
[b] *Departamento de Química Física i Analítica, UJI−Universitat Jaume I, Castelló de la Plana 12071, Spain - andres@qfa.uji.es*
[c] *Instituto de Química, UNESP, Araraquara 14800-900, Brazil - elson.liec@gmail.com*
[d] *Instituto de Física, Unicamp, Campinas 13083-970, Brazil - zacarias@ifi.unicamp.br*

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INTRODUCTION

The formation and growth of metallic Ag on α-Ag_2WO_4 upon electron beam irradiation is a novel process that has been investigated extensively by different experimental techniques including transmission electron microscopy (TEM), field emission scanning electron microscopy (FE-SEM), energy dispersive spectroscopy (EDS) characterization, among others[1-3]. This is a widely employed route to produce efficient photocatalysts, ozone sensors and bactericides.

METHODS

Quantum calculations based on the Density Functional Theory (DFT) using the VASP code were carried out on periodic supercells to represent the (100) and (001) surfaces of α-Ag_2WO_4. The geometries were optimized using the conjugate gradient (CG) method and selected structures were also studied using *ab initio* molecular dynamics simulations in the canonical ensemble at 300 K. The Nudged Elastic Band (NEB) method was used to characterize the minimum energy pathways for the diffusion process of Ag atoms.

RESULTS AND DISCUSSION

The nucleation and formation of metallic Ag on α-Ag_2WO_4 is initiated when Ag atoms diffuse from the interior material to the surface. In this work, we have made use of DFT calculations and *ab initio* molecular dynamics simulations to investigate the geometrical and electronic structure of the most favorable surfaces: (100) and (001). This semiconductor exhibits a complex structure, which can be understood as an arrangement of AgO_x (x = 2, 4, 6, and 7) clusters used as constituent building blocks. Thus, the relaxation process upon cleaving the surfaces from the bulk can induce significant rearrangements. We also show that there are specific Ag atoms in the sub-surface positions that are prone to undergo the diffusion process with very low energy barrier (< 0.1 eV). Furthermore, our results point out that the injection of electrons decreases the activation barrier for this diffusion step [4].

CONCLUSIONS

Our calculations supply an atomistic approach to the local geometry and the electronic structure of the surfaces exposed to the electron beam irradiation and gain insight into the initial stages of the metallic Ag growth on the Ag_2WO_4 surfaces.

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